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The Reduction of Ytterbium (III) to Ytterbium (II)

Amanda S. Jones
University of Tennessee - Knoxville

To the Graduate Council:

I am submitting herewith a thesis written by Amanda S. Jones entitled "The Reduction of Ytterbium (III) to Ytterbium (II)." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

George K. Schweitzer, Major Professor

We have read this thesis and recommend its acceptance:

Jamie L. Adcock, Michael J. Sepaniak

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

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and recommend its acceptance:

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Accepted for the Council:
Linda Painter
Interim Dean of the Graduate School

(Original Signatures are on file with official student records.)

THE REDUCTION OF YTTERBIUM (III)

TO YTTERBIUM (II)

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Amanda Shirlene Jones

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ABSTRACT

If Yb(III) could be reduced to the highly unstable Yb(II), and temporarily stabilized, the separation of Yb from the other lanthanide elements could be facilitated. This facilitation would be based upon the considerably different chemistry of Yb(II) from the trivalent forms of all other lanthanides.

The reduction of Yb(III) to Yb(II) using Mg was attempted in various media. The effects of the media, precipitating agent, and environment were examined. The best experimental conditions for the reduction of Yb(III) to Yb(II) and the subsequent precipitation of $YbSO_4$ were found to be the addition of ~0.35 g $YbCl_3 \cdot 8H_2O$ in 1.5 mL 3:1 ethanol:dioxane and 0.05 mL 17.4 M acetic acid to 0.15 g tetramethylammonium sulfate and ~0.20 g of 50 mesh Mg powder under nitrogen and over ice. Under these conditions, a maximum of 85% of the Yb(II) could be removed from the system.

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Chapter 1

INTRODUCTION

A. Introduction

One of the best, if not the best, scintillation detectors for high energy photons (X-rays or gamma rays) is lutetium oxysilicate, Lu_2OSiO_4, in its crystalline form.[1] This capability is due to its high density, high atomic number, efficiency for converting absorbed energy into visible light, and its very short light pulses. For optimum performance, the Lu involved in the production of Lu_2OSiO_4 must be 99.999% pure.

Lutetium is the highest atomic number element among the lanthanides (rare earth elements), all of which occur together in nature, since they exhibit a very similar chemistry based on their trivalent character.[2] The two rare earths Ce and Eu can be easily separated in aqueous solution from the others by redox reactions, Ce being oxidized from Ce(III) to Ce(IV) [E° (Ce^{+4}/Ce^{+3}) = 1.70 V][3], and Eu being reduced from Eu(III) to Eu(II) [E° (Eu^{+3}/Eu^{+2}) = -0.34 V][3]. All others show a very stable trivalent state in aqueous solution, and because of their extreme similiarity, require multi-staged separation processes. This is generally accomplished by lengthy ion-exchange columns or multi-staged counter-current solvent extraction systems[4], the latter being industrially preferred.

To separate 99.999% pure Lu, eighty or more stages of counter-current solvent extractions are required using an aqueous/organic system with an organically substituted phosphoric acid.[5] The element adjacent to Lu, namely Yb, is the one most difficult to separate. If, by some simple (one-stage) process, one could remove the Yb, partially or entirely, the production of pure Lu would be facilitated. Should the Yb be completely

removed, only about twenty stages of counter-current solvent extraction would be needed.

As will be chronicled below, Yb(III) has been shown to be partially reducible to Yb(II) in non-aqueous media and in some miscible aqueous/non-aqueous media containing small amounts of water. The chemistry of Yb(II) is radically different from the chemistries of Yb(III) and Lu(III), and hence partial separations of Yb and Lu have been reported. These partial, rather than complete, separations of Yb could be due to the very short life of Yb(II) in the presence of water and/or oxygen [E° (Yb^{+3}/Yb^{+2}) = ~ -1.1 V][3]. Some investigations have reported that Yb(II) in water can be somewhat stabilized by the addition of sodium tetraphenylborate.

B. History

Yb(II) was first prepared by Klemm and Schuth in 1929. Solid Yb_2O_3 was treated with a stream of Cl_2-S_2Cl_2 at a temperature of approximately 600 ºC to form solid $YbCl_2$. However, this was not a solution technique.[6]

In 1930, L.F. Yntema and R.W. Ball were able to reduce Yb(III) to Yb(II) and produce $YbSO_4$. A heavy rare earth chloride solution was prepared by dissolving 10 g of rare earth oxides in HCl, evaporating the excess, diluting the solution to 400 mL, and adding 4 mL of H_2SO_4. An electrolytic cell was set up to contain a Hg cathode and the rare earth solution in the cathode compartment and 0.05 N HCl and a Pt anode in the anode compartment. A current of 0.10 A, a current density of 0.025 A/cm^2 at the cathode, and a voltage of 110 V between electrodes was used. This resulted in the precipitation of $YbSO_4$. Yntema and Ball reported $YbSO_4$ was stable in acid solution

only when the current was applied and when the cathode had a high overvoltage. The authors also reported the purity of the Yb(II) separated from a mixed group of heavy earths was 98%; however, the original percentage of Yb(III) in the material was only 2%. A percent recovery of the Yb as the Yb(II) species was not reported.[7]

W. Prandtl made the next attempt to produce Yb(II) in solution in 1932. The redox preparation of $YbSO_4$ was based on the previous work done by Yntema and Ball. The electrolytic reduction was carried out in an aqueous solution of the heavy rare-earth sulfates using a Hg cathode and a Pt anode. The current was between 0.20 and 0.40 A, the voltage drop was 110 V, and the temperature ranged from 40 to 60 ºC. The purity and percent recovery of the $YbSO_4$ was not reported.[8]

In 1936, D.W. Pearce, C. R. Naesar, and B.S. Hopkins also reduced Yb(III) using a Hg cathode and a Pt anode. The anode consisted of a piece of Pt foil that was inserted in a glass tube that was turned upward to form a hook, and the Hg cathode was enclosed in a cone-shaped tube. The anode compartment was located within the cathode compartment, which was surrounded by a water jacket to control temperature. Hydrated $YbCl_3$ (0.40 N) was dissolved in 1.2 N sulfuric acid, and the reduction was carried out by applying a voltage of 110 V and a current density of 0.16 A/cm^2. Due to a partial decomposition of $YbSO_4$ when the current was no longer applied, a complete reduction was not obtained, as approximately 10% of the Yb remained in solution. The authors reported that the low temperature aided in removing small amounts of Yb from large amounts of Lu or Tm.[9]

J.K. Marsh produced $YbSO_4$ electrolytically by using an amalgamated Pb cathode and a lead pipe anode in 1937. The electrolytic cell consisted of a porous pot placed into

a 400 mL beaker. The porous pot contained the anode and 2 N sulfuric acid and the beaker contained the cathode and $Yb_2(SO_4)_3$ solution (~0.03 M), prepared from a reaction of Yb_2O_3 and 2 N sulfuric acid. Six of these cells were set up in a series, and a voltage of 100 V with a cathode current density of 0.30 A/cm^2 was applied to the system. Marsh reported 95% of the Yb was recovered as $YbSO_4$ if pure lead was used and that four precipitations of $YbSO_4$ raised the purity from 30% to 100%. He also reported Yb(II) was more stable if the starting solution did not contain any traces of heavy metals.[10]

Later that year, A. Brukl discovered further precipitation of $YbSO_4$ could be achieved with the addition of $SrCO_3$ to a solution containing H_2SO_4 using a Hg cathode. $SrSO_4$ formed in the solution from the reaction of H_2SO_4 with $SrCO_3$, and $YbSO_4$ co-precipitated with the $SrSO_4$, but 100% of the Yb(II) was not recovered. This was said to be due to the solubility of the $YbSO_4$, not an incomplete reduction of Yb(III) to Yb(II).[11]

L. Holleck and W. Noddack developed a new method for preparing divalent rare earths in 1937 using a Sr amalgam. A Sr amalgam was placed in an aqueous Yb(III) sulfate solution. The Yb(III) was reduced to Yb(II) and concurrently produced $YbSO_4$. The Sr was oxidized to Sr (II) and produced $SrSO_4$ simultaneously. The co-precipitation of $YbSO_4$ and $SrSO_4$ allowed for the stabilization of the Yb(II). The authors reported an 80% recovery of Yb as Yb(II).[12]

The following year, L. Holleck stated that the formation of divalent compounds is a property of all rare earth elements. He examined the reducibilities of the rare earth chlorides of the lanthanides as well as Sc and Y. The dehydrated salts were heated in a stream of H_2 to produce both the metal and the dichloride. The reducibility to the metal increased from La to Lu, but Sm, Yb, and Eu only gave the stable dichloride.[13]

In 1940, G.C. Walters and D.W. Pearce reported the first value of the Yb(III) / Yb(II) electrode potential as -0.578 V using a Pt indicator electrode.[14] However, H.A. Laitinen disagreed with this value, as erroneous results were usually obtained with the Pt indicator electrode because of mixed potential behavior in the Yb(III) and Yb(II) salt solutions. In 1942, he performed a similar study with a dropping mercury electrode, reporting an electrode potential between -1.05 and –1.17 V and a half wave potential of –1.15 V.[15] At the time, this was accepted as the most probable potential for the Yb(III) / Yb(II) couple. However, some later investigations introduced some ambiguity in the exact value of the reduction potential. The following authors used polarographic results to recommend their values of the reduction potential. In 1974, D.A. Johnson reported a value of –1.10 V for the couple.[16] L.R. Morss estimated the value to be –1.04 V in 1976.[17] In 1988, D. Ferri *et al.* estimated the value of the potential in 3M NaCl to be –1.155 V.[18]

M. Peltier and P. Rombau were able to separate the trivalent and divalent rare earth ions in 1960 by using NH_4OH. Also, by using the same system, addition of sulfate resulted in the precipitation of the divalent rare earth as $LnSO_4$ and the trivalent rare earth as $Ln(OH)_3$. Acidification of the mixture dissolved the trivalent lanthanide and the divalent lanthanide sulfate was separated by filtration.[19]

In 1963, L.B. Asprey, F.H. Ellinger, and E. Staritzky precipitated $YbSO_4$ over a Hg pool cathode. An electrolytic cell was set up to contain a Hg cathode and a Pt anode. The cathode compartment contained a 30 mil W wire immersed in a capillary containing Hg and 0.1 M $Yb_2(SO_4)_3$ solution in 0.1 M acetic acid at a pH of 5.5. The anode consisted of 20 mil Pt wire that was coiled into a spiral and flattened. During electrolysis, the

anode tube was dipped into the rare earth solution. A current density between 0.02 and 0.06 A/cm^2 and a voltage between 6 and 12 V were used. The current flow was adjusted by changing the voltage. The authors observed the formation of $YbSO_4$ within a few minutes. Solid $YbSO_4$ was removed from the system by pipet, centrifuged, and the crystals were washed with water, then acetone, and allowed to dry. This treatment allowed the $YbSO_4$ to be stable in air for several days. The sulfate crystals were further reacted with carbonate and fluoride in order to obtain measurements of optical properties and crystal structures of the resulting compounds. However, due to the instability of the divalent salts, the precisions of the measurements were of poor quality, but still sufficient for characterization.[20]

B. Mikheev, *et al.* prepared Yb(II) chloride using Mg in 1972. A mixture of Sm(III) chloride, Eu(III) chloride and Yb(III) chloride was dissolved in an acidic aqueous ethanol solution and reduced using Mg. The authors discovered an isomorphous co-crystallization of $EuCl_2$ and $YbCl_2$ on the surface of the Mg, which they claimed was due to the formation of mixed crystals. A percent recovery of $YbCl_2$ was not reported.[21]

L.I. Maksai and M.G. Sayun produced $YbSO_4$ in 1974 by an amalgam method. A Yb amalgam was formed, added to a stirred chloride/acetate buffer solution containing Na_2SO_4 in an inert atmosphere, and after ten to fifteen minutes, $YbSO_4$ formed. The sulfate was rapidly filtered, washed with alcohol and ether, and then dried. The authors reported a 95.5% recovery of Yb as $YbSO_4$.[22]

In 1975, B.F. Myasoedov, *et al.* reported the reduction of Eu(III), Sm(III), Tm (III), Er(III) and Am(III) to the divalent state in acetonitrile using potential-controlled electrolysis and polarography. It was noted that the water that was present in the

acetonitrile attacked the divalent ions; thus, they were oxidized to the hydrolyzed trivalent cation during electrolysis. The stability and rate of oxidation were both dependent upon the cation.[23]

A.N. Kamenskaya, *et al.* reported in 1983 that the presence of sodium tetraphenylborate (NaTPB) contributes to the stabilization of divalent lanthanides in water. The various properties of aqueous and aqueous:ethanol solutions of Sm(II) and Yb(II) as well as the stabilization through the addition of NaTPB were examined. The authors reported the addition of NaTPB to Yb(II) in a 4:1 ratio increased the half-life from ten to fifteen minutes to more than 200 hours. A percent recovery of the Yb(II) was not reported.[24]

In 1992, I.E. Valeshko *et al.* used co-crystallization, conductance, and spectrophotometry to study the interaction of divalent lanthanides with NaTPB in acetonitrile and ethanol solutions. The authors reported that complexation occurs in both ethanol and acetonitrile.[25,26] It was noted that this complexation might follow several mechanisms, including tunneling charge transfer, charge transfer through groups of bonds of solvent in the first coordination sphere, and holding a ligand in the outer sphere through interaction with non-reactive hydrogen atoms of solvent consisting of the solvation sphere of the cation.[25]

T. Hanamoto, *et al.* reported the reduction of Sm(III) triflate and Yb(III) triflate to Sm(II) triflate and Yb(II) triflate in 1994. The trivalent compounds were dissolved in a solution containing tetrahydrofuran (THF) and ethylmagnesium bromide and allowed to react at room temperature. Hanamoto, *et al.* was interested in using the divalent complexes as catalysts in organic reactions.[27]

In 1998, J.D. Siler was able to reduce Yb(III) to Yb(II) in a 1:1 mixture of ethanol:dioxane. Mg powder was added to a solution of Yb(III) chloride forming a precipitate of Yb(II) chloride. The idea of using this system came from previous work performed by A.F. Clifford and H.C. Beachell in 1948.[28] They were able to reduce Sm(III) to Sm(II) in a 1:1 mixture of ethanol:dioxane saturated with $BaCl_2$ and $SrCl_2$ using Mg metal.[29]

R.J. Mack performed an electrolytic reduction of Yb(III) to Yb(II) using a Pb cathode in various media in 2000. A 0.11 M solution of $YbCl_3 \cdot 6H_2O$ in 1:1 ethanol:dioxane under a direct current of ~20 mA and a pH of 2 was reduced to Yb(II) and precipitated with a 3.0 M solution of $(NH_4)_2SO_4$. A maximum of 30% $YbSO_4$ was removed from the system.[30]

C. Proposed Research

The major observations which have been made on the production of Yb(II) in the presence of water are as follows:

(1) Most experimentation has been done on a lab scale. Little with the goal of an industrial process has been carried out.

(2) The most successful system, so far, involves the use of a Hg or an amalgam cathode. However, this is not industrially applicable because of health considerations.

(3) The use of Mg metal [E° (Mg^{+2}/Mg^0)= -2.36 V][31] can bring about the reduction if it is carried out in proper non-aqueous or aqueous/non-aqueous solvents.

(4) Aqueous/non-aqueous solvents are better because hydrated rare earth compounds can be used. These are much cheaper than anhydrous compounds that require specialized preparation and which hydrate rapidly upon exposure to air. The best solvent system consisted of ethanol, 1,4-dioxane, and a small amount of water.

(5) Once Yb(II) has been obtained in aqueous/non-aqueous media, the best means of separation has been precipitation of the slightly soluble $YbSO_4$ ($K_{sp}=10^{-3.7}$)[11]. Sulfates of the trivalent rare earth ions are more soluble.

The goal of this research is to develop a process for the industrial separation of Yb from all other rare earths, but especially Lu. Starting from the previous work, these lines of investigation were to be performed:

(1) Optimize the reduction of Yb(III) to Yb(II)

   a. vary the solvent system (EtOH, THF, CH_3CN, DMSO)
   b. vary form of the Mg metal, including ultrasonic treatment
   c. attempt stabilization with NaTPB
   d. vary anion of salts introduced
   e. vary temperature
   f. exclude oxygen

(2) Optimize the separation of Yb(II) from Ln(III)

   a. method of introduction of sulfate
   b. precipitation of $Ln(OH)_3$, but not $Yb(OH)_2$

c. common ion effect: saturate with Cl^- or SO_4^{-2}

d. solvent extraction with 2-ethylhexyl-mono(2-ethylhexyl)-ester phosphinic acid

Chapter 2

EXPERIMENTAL APPROACH

A. Basic System

The basis for this project was to remove Yb(III) from a mixture of rare earths in water solution by chemical reduction to Yb(II) using Mg, then separation from the trivalent rare earths by various chemical means.

B. Chemicals

The chemicals used in the experiments are listed in Table 1. The use of considerably pure reagents was very important because it is known that some redox reactions are strongly affected by impurities, especially those of heavy metals.

C. Apparatus

Three different types of apparatus were used throughout this research: (1) a test tube, (2) a modified test tube, and (3) a column. A description of each apparatus and its modifications are provided below.

(1) Test Tube

As an initial experiment, Yb(III)[as $YbCl_3 \cdot 8H_2O$ for example]and very small amounts of redox intermediate ions [such as Cu^{+2}, VO_3^-, WO_4^{-2}] were dissolved in water in a test tube. In another test tube, a Yb(II)-stabilizing agent [NaTPB] was dissolved in an organic medium [EtOH]. These solutions were combined into one test tube and a strip of abraded Mg ribbon was added.

Table 1: Chemicals

Chemical	**Supplier**	**Purity**
Water		deionized
Ethanol	Aaper Alcohol and Chemical Co.	95%, 190 proof
1,4-dioxane	Sigma Aldrich	99.8% anhydrous
Acetonitrile	Fisher Scientific Co.	HPLC grade, 99.9%
Tetrahydrofuran	Fisher Scientific Co.	Reagent grade, >99%
Light Mineral Oil	Fisher Scientific Co.	>99%
2-ethylhexyl-mono(2-ethylhexyl)-ester phosphinic acid	Albright & Wilson Americas	Ionquest 801
Dimethylsulfoxide	Fisher Scientific Co.	anhydrous, 99.7%
Kerosene	Sigma Aldrich	>99%
1,3-dioxolane	Acros	99%
Tetraphenylboron Sodium	Acros	ACS reagent grade, 99.5%
Sodium metavanadate	Sigma Aldrich	96%
Copper Sulfate	Fisher Scientific Co.	anhydrous, 98%
Sodium tungstate	Fisher Scientific Co.	certified ACS, >98%
Sodium sulfate	Sigma Aldrich	ACS reagent grade, 99+%
Vanadyl sulfate	Sigma Aldrich	$\geq$99%
Magnesium sulfate	Mallinckrodt	Analytical reagent, 99%
Potassium permanganate	Fisher Scientific Co.	certified ACS, $\geq$99%
Barium chloride	Mallinckrodt	Analytical reagent, $\geq$97%
Strontium chloride hexahydrate	Matheson, Coleman & Bell	Analytical reagent, $\geq$99%
Sodium sulfite	Sigma Aldrich	anhydrous, 98+%
Ammonium sulfate	Fisher Scientific Co.	>99%

Table 1: Continued

Chemical	**Supplier**	**Purity**
Tetramethylammonium sulfate (TMAS)	TCI Chemicals	≥99%
Tetramethylammonium methyl sulfate (TMAMS)	Acros	≥99%
Tetraethylammonium hydrogen sulfate (TEAHS)	Fluka Chemie	≥99%
Tetrabutylammonium hydrogen sulfate (TBAHS)	Acros	98%
Lead nitrate	JT Baker Chemical Co.	>99%
Potassium chloride	Fisher Scientific Co.	≥99%
Lutetium (III) Chloride hexahydrate	Sigma Aldrich	99.99+%
Ytterbium (III) chloride hexahydrate	Sigma Aldrich	99.9%
Ytterbium (III) chloride hexahydrate	GFS Chemicals	99.9%
Hydrochloric acid	Fisher Scientific Co.	certified ACS plus, 99.95%
Sulfuric acid	Fisher Scientific Co.	certified ACS plus, 90-98%
Acetic acid, glacial	Fisher Scientific Co.	certified ACS plus, >96%
Nitric acid	Fisher Scientific Co.	certified ACS plus, 99.95%
Magnesium ribbon	Fisher Scientific Co.	99+%
Magnesium powder	Sigma Aldrich	50 mesh, ≥ 99% Reagent plus

Modifications of the above procedure were then pursued. The first such modification included omitting the redox ions, carrying out the experiment in one test tube, and varying the organic solvent [THF, 1,3-dioxolane, CH_3CN, 1,4-dioxane]. Further changes to this system included ultrasonic treatment and replacing Mg ribbon with Mg powder.

Previous experiments showed the addition of Mg powder to a mixture containing Yb(III) dissolved in EtOH and 1,4-dioxane resulted in a light green solution containing Yb(II). The next modification to the system involved the addition of Yb(II) to another test tube containing a sulfate precipitating agent [Na_2SO_4, $(NH_4)_2SO_4$, Na_2SO_3, TMAMS, TMAS] dissolved in ethanol, 1,4-dioxane, and water. The system was further modified by performing the experiment in a glove bag filled with nitrogen.

The next variation in the research was dissolving Yb(III) in a test tube containing ethanol, 1,4-dioxane, and acid. The solution was then added to another test tube containing TMAS and Mg powder, which was covered with a septum and flushed with nitrogen. Figure 1 is an illustration of this setup. This system was further modified by performing the reaction over dry ice and then ice. Additional variations included connecting a gas dispersion tube to a syringe through the septum. Figure 2 is an illustration of this setup.

(2) Modified Test Tube

Attempts were made to upscale and simplify the above setup. Yb(III) was dissolved in a test tube containing ethanol, 1,4-dioxane, and acid. The solution was then added to a 25 mL 3-neck (each opening covered with a septum) round-bottom flask

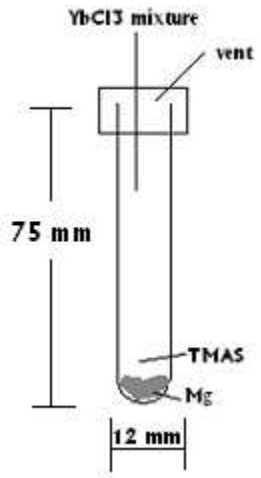

Figure 1: Simple System Setup

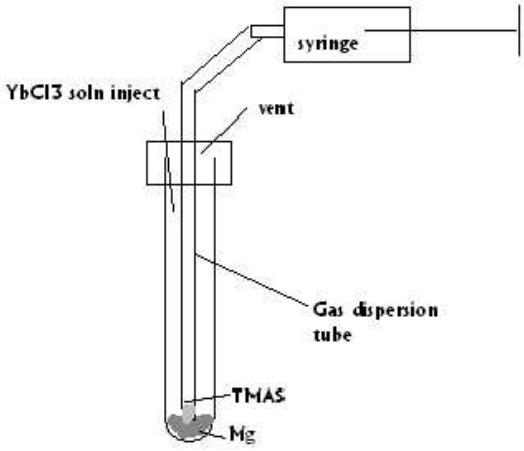

Figure 2: Sealed Setup with Syringe and Gas Dispersion Tube

containing a small amount of Mg powder and TMAS, and flushed with nitrogen. A gas dispersion tube and syringe were connected and fed through the middle septum. Experiments using this setup were performed over ice. Figure 3 is an illustration of this setup. The apparatus was further modified by attaching a portion of a test tube (1 ½" in length) to the bottom of the flask. Figure 4 is an illustration of this setup. The final modification to this setup was using a smaller apparatus. A 15 mL 3-neck (each opening covered with a septum) round-bottom flask with a portion of a test tube (1 ½" in length) attached was made. Experiments were performed as previously stated.

(3) Column

A Mg column was another apparatus that was employed during this research. An 8" glass buret was filled with approximately 5" of Mg powder, which was covered with a balloon filled with nitrogen. The tip of the column was attached to a filter flask through a one-hole rubber stopper and the flask was hooked up to an aspirator. A small amount of solid TMAS was added to the flask and a solution containing Yb(III) dissolved in ethanol, 1,4-dioxane, and acid was added to the column. Figure 5 is an illustration of this setup. The next modification to this system was adding a septum to the top of the column and covering the opening of the filter flask with a balloon filled with nitrogen. A needle connected to a nitrogen line was inserted through the septum. Figure 6 is an illustration of this setup. The final modification to this setup was affixing two plastic T's that were fused together to the column, through the septum. This created three in-/outlets which allowed one to flush the column with nitrogen, load Yb(III) solution, and vent for pressure build-up due to the evolution of H_2. Figure 7 is an illustration of this setup.

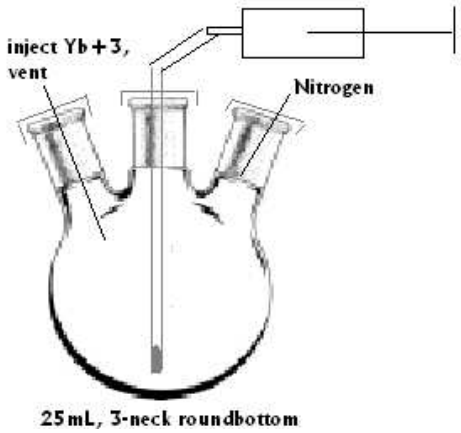

Figure 3: Sealed Setup Using 3-neck Round Bottom Flask

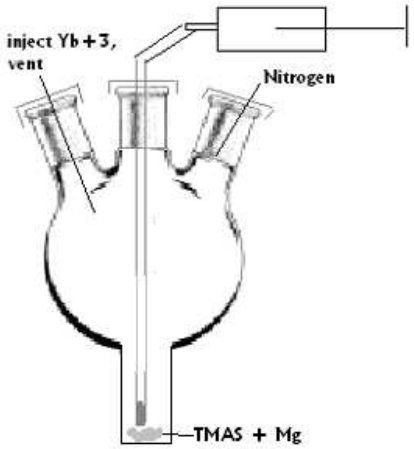

Figure 4: 3-neck Round Bottom Flask with Test Tube Attached

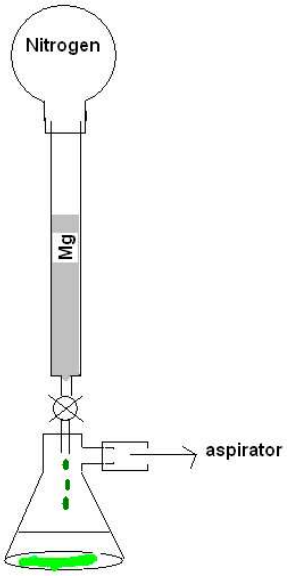

Figure 5: Initial Mg Column Setup

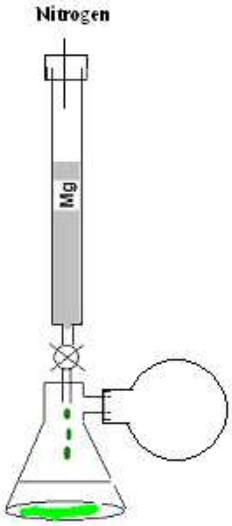

Figure 6: Second Mg Column Apparatus

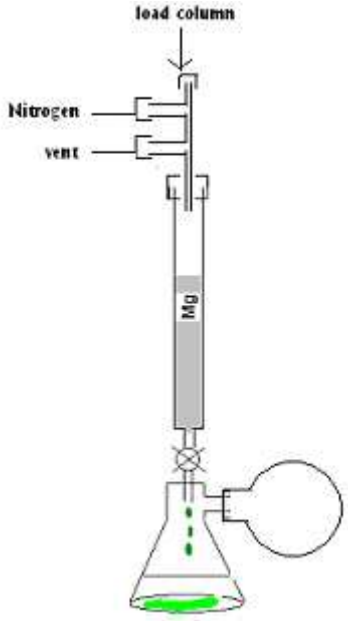

Figure 7: Third Mg Column Apparatus

D. Analysis

The Yb and Lu ion concentrations were determined by atomic emission spectroscopy. The spectrometer used was a Perkin Elmer AAnalyst 100. The analyses were performed at a wavelength of 398.8 nm for Yb and 336.0 nm for Lu. All standards were prepared by diluting 1000 ppm SpecPure AAS standards. For each experiment, the solid and liquid were separated by centrifugation and analyzed for the appropriate rare earth. KCl (0.1% w/v) was added to each sample in order to reduce the possibility of ionization interferences. If necessary, sample dilutions were performed and were dependent on the individual rare earth and its linear spectroscopic determination range. A percent recovery was calculated by comparing the concentrations of each solid and liquid.

Chapter 3

EXPERIMENTAL RESULTS

Indications in the literature and some rough experiments in the laboratory provided some useful hints about where this research should begin. On the basis of this, an initial experiment was designed. In this initial experiment, Yb(III)[as $YbCl_3 \cdot 8H_2O$ for example]and very small amounts of redox intermediate ions [such as Cu^{+2}, VO_3^-, WO_4^{-2}] were dissolved in water in a test tube. In another test tube, a Yb(II)-stabilizing agent [NaTPB] was dissolved in an organic medium [EtOH]. These solutions were combined into one test tube and a strip of abraded Mg ribbon was added. Experiments I-1 through I-4 were performed in a sulfate solution and experiments I-5 through I-11 were performed in a chloride solution. Each of these experiments had a different amount of one of the components. This was done during the investigation to see which combination yielded the highest amount of Yb(II) recovered in the solid phase. The amounts and concentrations of each reagent used in the sulfate system and the chloride system are found in Table 2 and Table 3, respectively. Each reaction was performed in triplicate and was allowed to react untouched for approximately 12 hours. Positive results for Yb(II) yielded a light green precipitate. AE analysis was performed on each sample and the % Yb recovered in the solid phase is found in either Table 2 or Table 3.

Experiments I-1 through I-4 and I-9 and I-11 were repeated, as they proved to be the most successful ($\geq$ 97%). For each of these experiments, a reddish-brown precipitate, with no evidence of Yb(II) formed. An extensive investigation was performed to determine what caused these previously successful experiments to fail. The first variable

Table 2: Yb(III) reduction with redox ions in sulfate system.

Components	**I-1**	**I-2**	**I-3**	**I-4**
Volume 0.2 M VO_3^- in 0.5 M H_2SO_4 (µL)	120	120	120	120
Volume 0.2 M Cu^{+2} (µL)	80	80	80	80
Volume 0.0025 M WO_4^{-2} (µL)	40	40	40	80
Volume 2.5 M Na_2SO_4 (µL)	40	0	40	0
Volume 95% EtOH (µL)	280	280	280	280
Mass NaTPB (g)	0.008	0.008	0.004	0.006
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.004	0.004	0.004	0.006
% Yb recovered in solid phase	99	99	99	97

Table 3: Yb(III) reduction with redox ions in chloride system.

Components	**I-5**	**I-6**	**I-7**	**I-8**	**I-9**	**I-10**	**I-11**
Volume 0.2 M VO_3^- in 0.9 M HCl (µL)	1200	1200	1200	1200	1200	1200	1200
Volume 0.2 M Cu^{+2} (µL)	800	800	600	700	900	800	800
Volume 0.0025 M WO_4^{-2} (µL)	400	400	600	500	300	400	400
Volume 95% EtOH (µL)	2400	2400	2400	2400	2400	2400	2400
Mass NaTPB (g)	0.08	0.04	0.08	0.04	0.08	0.008	0.008
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04	0.04	0.04	0.004	0.04
% Yb recovered in solid phase	47	42	62	16	99	99	99

Table 4: Yb (III) reduction with omission of single redox ions in chloride system.

Components	**I-11**	**I-12**	**I-13**	**I-14**
Volume 0.2 M VO_3^- in 0.2 M HCl (µL)	1200	1200	0	1200
Volume 0.2 M Cu^{+2} (µL)	800	800	800	0
Volume 0.0025 M WO_4^{-2} (µL)	0	400	400	400
Volume 95% EtOH (µL)	2400	2400	2400	2400
Mass NaTPB (g)	0.08	0.08	0.08	0.08
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04	0.04

examined was the use of conditions as before, with the omission of the redox ions [VO_3^-, Cu^{+2}, WO_4^{-2}] in separate experiments (I-12 through I-15). Table 4 shows the components of each reaction. Each of the experiments produced a clear, peach solution with a light grey precipitate. Temperature was the second variable investigated. Reactions I-1 through I-4 and I-9 through I-11 were repeated in an ice bath to see if slowing the reaction produced Yb(II). However, there was no evidence of the formation of Yb(II). These reactions were also performed in a warm water bath (~90 ºC) to see how heat affected the reduction. Once again, there was no evidence of Yb(II).

After the initial set of successful experiments, a new solution of VO_3^- was prepared. Great difficulty was experienced in the preparation of this solution. A reddish-brown precipitate, which is likely V_2O_5, would immediately fall out of solution. Changes were made to the preparation of this solution to keep this from happening. A stronger concentration of acid prevented the formation of V_2O_5 and produced a clear, bright yellow solution. However, use of this solution did not allow for the reduction of Yb(III) toYb(II). Over fifty attempts were made to produce a VO_3^- solution that did not precipitate V_2O_5 and with which reactions produced a green Yb(II) precipitate. Furthermore, different forms of V were used to see if success could be achieved. A 0.2

M solution of vanadyl sulfate ($VOSO_4$) in 0.5 M H_2SO_4 was prepared and used instead of VO_3^- in reactions I-1 through I-4 and I-9 through I-11. Each of these experiments resulted in a reddish-grey precipitate, with no evidence of Yb(II).

The final variable examined was the elimination of all of the redox ions. The components of these reactions (I-16 through I-18) are listed in Table 5. Each reaction was performed in triplicate at room temperature for approximately 12 hours. Each resulted in a green precipitate, which we suspect is Yb(II) as the chloride. This was verified by adding a drop of dilute $KMnO_4$ to the precipitate, the bleaching of which showed a reduced species to be present. Reactions I-16 through I-18 were repeated, as they appeared to be successful. Each reaction resulted in a green precipitate, presumably Yb(II) as the chloride. AE analysis was performed on each sample and the average % Yb recovered in the solid phase is found in Table 5. This system was further investigated, by varying the amounts and concentrations of the components, to see if the amount of Yb(II) recovered in the solid phase could be increased. Table 6 shows the components of each reaction and the % Yb recovered. Each reaction was performed in triplicate and allowed to react at room temperature for 36 hours. Each reaction resulted in the formation of a green precipitate, likely Yb(II) as the chloride.

Table 5: Yb (III) reduction without redox ions.

Comonents	**I-16**	**I-17**	**I-18**
Volume 95% EtOH (µL)	2400	3000	2400
Volume 0.2 M HCl (µL)	300	600	300
Mass NaTPB (g)	0.08	0.08	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
% Yb recovered in solid phase	66	39	43

Table 6: Additional Yb(III) reduction reactions without redox ions.

Components	**I-19**	**I-20**	**I-21**
Volume 95% EtOH (µL)	2500	5000	2500
Volume 1.0 M HCl (µL)	300	600	300
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.06
% Yb recovered in solid phase	68	72	65

Table 7: Yb(III) reduction timed trials.

Sample	**% Yb recovered in solid phase**
I-22 (24h)	70
I-23 (36h)	84
I-24 (48h)	62
I-25 (60h)	69
I-26 (72h)	65

Time was the next variable examined to see if the amount of Yb(II) recovered could be increased. Reactions containing the same components as I-20 were set up in triplicate and allowed to react at room temperature for 24, 36, 48, 60, and 72 hours. Each reaction produced a green precipitate, likely Yb(II) as the chloride. AE analysis was performed on each sample and the amount of Yb recovered is listed in Table 7.

Reaction I-23 proved to be the most successful of the timed reactions. Therefore, this reaction was repeated, in triplicate, to determine its reproducibility. Each reaction produced a green precipitate with approximately 86% Yb. Additional reactions were performed with varying amounts of reagents. The most successful system was performed at room temperature for 36 hours and contained 3 mL ethanol, 0.3 mL 1 M HCl, 0.04 g $YbCl_3 \cdot 8H_2O$, 0.04 g NaTPB, and a strip of abraded Mg ribbon (I-27). Each reaction produced a green precipitate with approximately 96% Yb.

Further modifications to this system included the addition of Na_2SO_4 in order to precipitate $YbSO_4$. This proposed change should be a feasible separation process, as Mg has the potential to reduce Yb(III) to Yb(II) but not Lu(III) to Lu(II). The addition of sulfate to the system would result in the precipitation of $YbSO_4$ and $Lu_2(SO_4)_3$ might remain soluble. The initial system contained 3 mL 95% EtOH, 0.3 mL 1 M Na_2SO_4, 0.3 mL 1 M HCl, 0.04 g $YbCl_3 \cdot 8H_2O$, 0.04 g NaTPB, and a strip of abraded Mg ribbon (I-28). This reaction was performed in triplicate and allowed to react at room temperature for 36 hours. Each sample resulted in the formation of a white precipitate. Further deviations to this system involved varying the amounts and concentrations of the components. Table 8 lists the components of each of these reactions and the observations after 36 hours. All of the reactions produced a white precipitate that was deemed to be $Yb_2(SO_4)_3$. This induced an experiment to determine whether this precipitate was, in fact, $Yb_2(SO_4)_3$. A reaction was performed, like the previous one, except the reduction step was omitted. A white precipitate formed immediately, indicating $Yb_2(SO_4)_3$ was insoluble in this medium.

Due to the immediate precipitation of $Yb_2(SO_4)_3$, the next modification to the system was to first produce Yb(II) as the chloride, add Na_2SO_4, and then stir. Yb(II), as

Table 8: Yb(III) reduction with addition of Na_2SO_4.

Components	**I-29**	**I-30**	**I-31**
Volume 95% EtOH (mL)	3.00	3.00	0.60
Volume 1.0 M HCl (mL)	0.30	0.30	0.30
Volume 0.5 M Na_2SO_4	0.30	0.15	0.15
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
Observations	white precipitate	tan precipitate	white precipitate

the chloride, was first prepared by allowing 3 mL 95% EtOH, 0.3 mL 1 M HCl, 0.04 g $YbCl_3 \cdot 8H_2O$, 0.04 g NaTPB, and a strip of abraded Mg ribbon to react at room temperature for 36 hours. Each reaction using these components resulted in a colorless solution and a green precipitate. The solid and liquid were separated via centrifugation and the supernatant removed. Varying amounts and concentrations of Na_2SO_4 solution were added to the precipitate and allowed to stir for one week at room temperature. A time frame of one week was used to allow for a complete reaction to occur. The components and % Yb recovered in the solid phase are included in Tables 9, 10, and 11. Each reaction resulted in a more intense green precipitate, which was more intense than any that had been seen before.

Table 9: Yb(III) reduction and then, addition of 0.1 M Na_2SO_4.

Components	**I-32**	**I-33**	**I-34**
Volume 95% EtOH (mL)	3.00	3.00	3.00
Volume 1.0 M HCl (mL)	0.30	0.30	0.30
Volume 0.1 M Na_2SO_4 (mL)	1.00	2.00	3.00
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
% Yb recovered in solid phase	66	68	62

Table 10: Yb(III) reduction and then, addition of 0.5 M Na_2SO_4.

Components	**I-35**	**I-36**	**I-37**
Volume 95% EtOH (mL)	3.00	3.00	3.00
Volume 1.0 M HCl (mL)	0.30	0.30	0.30
Volume 0.5 M Na_2SO_4 (mL)	1.00	2.00	3.00
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
% Yb recovered in solid phase	78	74	82

Table 11: Yb(III) reduction and then, addition of 1.0 M Na_2SO_4.

Components	**I-38**	**I-39**	**I-40**
Volume 95% EtOH (mL)	3.00	3.00	3.00
Volume 1.0 M HCl (mL)	0.30	0.30	0.30
Volume 1.0 M Na_2SO_4 (mL)	1.00	2.00	3.00
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
% Yb recovered in solid phase	92	91	94

Table 12: Lu(III) and then, addition of 1.0 M Na_2SO_4

Components	**I-41**	**I-42**	**I-43**
Volume 95% EtOH (mL)	3.00	3.00	3.00
Volume 1.0 M HCl (mL)	0.30	0.30	0.30
Volume 1.0 M Na_2SO_4 (mL)	1.00	2.00	3.00
Mass NaTPB (g)	0.04	0.04	0.04
Mass $LuCl_3 \cdot 6H_2O$ (g)	0.0037	0.0037	0.0037
% Lu in solid phase	88	93	92

Due to the large percent recovery of Yb in the solid phase, the feasibility of the separation process was examined. Reactions I-38, I-39, and I-40 were performed with $LuCl_3 \cdot 6H_2O$ instead of $YbCl_3 \cdot 8H_2O$. The amount of $LuCl_3 \cdot 6H_2O$ added was 1/10 the molar amount of $YbCl_3 \cdot 8H_2O$ because of its natural abundance. Table 12 contains the components of the reactions with $LuCl_3 \cdot 6H_2O$ and the % Lu that remained in solution. Each reaction resulted in a tan precipitate. According to Table 12, very small amounts of Lu are being retained in the liquid phase, suggesting $Lu_2(SO_4)_3$ is highly insoluble in this medium.

The next modification to this research was experimenting with various organic solvents in lieu of or in addition to EtOH. Each reaction was performed in triplicate, contained 3 mL solvent, 0.3 mL acid, 0.04 g $YbCl_3 \cdot 8H_2O$, 0.04 g NaTPB, and a strip of abraded Mg ribbon, and was allowed to react at room temperature for 36 hours. Table 13

Table 13: Yb(III) reduction in various solvents.

Sample	Solvent(s)	Ratio	Acid	Observations
I-44	EtOH	1	HCl	green precipitate
I-45	EtOH	1	HOAc	brown precipitate
I-46	EtOH:CH_3CN	1:1	HCl	grey precipitate
I-47	EtOH:CH_3CN	1:1	HOAc	white precipitate
I-48	EtOH:CH_3CN	2:1	HCl	grey-green gel
I-49	EtOH:CH_3CN	2:1	HOAc	white precipitate
I-50	EtOH:CH_3CN	1:2	HCl	grey-green precipitate
I-51	EtOH:CH_3CN	1:2	HOAc	reddish-brown precipitate
I-52	EtOH:H_2O	1:1	HCl	tan precipitate
I-53	EtOH:H_2O	1:1	HOAc	white precipitate
I-54	EtOH:H_2O	2:1	HCl	green precipitate
I-55	EtOH:H_2O	2:1	HOAc	white precipitate
I-56	EtOH:H_2O	1:2	HCl	tan precipitate
I-57	EtOH:H_2O	1:2	HOAc	white precipitate
I-58	EtOH:THF	1:1	HCl	tan precipitate
I-59	EtOH:THF	1:1	HOAc	green precipitate
I-60	EtOH:THF	2:1	HCl	white precipitate
I-61	EtOH:THF	2:1	HOAc	white precipitate
I-62	EtOH:THF	1:2	HCl	white precipitate
I-63	EtOH:THF	1:2	HOAc	white precipitate
I-64	CH_3CN	1	HCl	brown-green precipitate
I-65	CH_3CN	1	HOAc	brown precipitate
I-66	CH_3CN:H_2O	1:1	HCl	brown-green precipitate
I-67	CH_3CN:H_2O	1:1	HOAc	grey-tan precipitate
I-68	CH_3CN:H_2O	2:1	HCl	brown precipitate
I-69	CH_3CN:H_2O	2:1	HOAc	brown precipitate
I-70	CH_3CN:H_2O	1:2	HCl	tan precipitate
I-71	CH_3CN:H_2O	1:2	HOAc	grey precipitate
I-72	CH_3CN:THF	1:1	HCl	brown precipitate
I-73	CH_3CN:THF	1:1	HOAc	brown precipitate
I-74	CH_3CN:THF	2:1	HCl	tan precipitate
I-75	CH_3CN:THF	2:1	HOAc	tan precipitate
I-76	CH_3CN:THF	1:2	HCl	tan precipitate
I-77	CH_3CN:THF	1:2	HOAc	grey precipitate
I-78	THF	1	HCl	tan precipitate
I-79	THF	1	HOAc	white precipitate
I-80	THF:H_2O	1:1	HCl	white precipitate
I-81	THF:H_2O	1:1	HOAc	white precipitate
I-82	THF:H_2O	2:1	HCl	white precipitate
I-83	THF:H_2O	2:1	HOAc	white precipitate

Table 13: Continued

Sample	Solvent(s)	Ratio	Acid	Observations
I-84	THF:H_2O	1:2	HCl	white precipitate
I-85	THF:H_2O	1:2	HOAc	white precipitate

Table 14: AE analysis for successful experiments (I-44 through I-85).

Sample	% Yb in solid phase
I-44	84
I-50	61
I-54	76
I-59	80
I-64	97
I-66	90

contains the additional components of each reaction and the observations. AE analysis was performed for those reactions that resulted in a green precipitate, likely Yb(II) as the chloride, and those are listed in Table 14.

Reaction I-64 proved to be the most successful, as 97% Yb was recovered in the solid phase. The next modification to this research was focused on using acetonitrile as the organic solvent. The components of reaction I-64 were varied to see if the amount of Yb recovered could be increased. These variations and the % Yb recovered in the solid phase are listed in Table 15. Each reaction was performed in triplicate and allowed to react for 36 hours, and each resulted in the formation of a green precipitate.

The acetonitrile system was very successful and was further examined by using acetic acid instead of hydrochloric acid. The components and % Yb recovered are listed in Table 16. The use of acetic anhydride instead of acid was also another variable explored. Acetic anhydride was employed to see how the system behaves with less water

Table 15: Yb(III) reduction in CH_3CN with HCl.

Components	**I-86**	**I-87**	**I-88**
Volume CH_3CN (mL)	3.00	3.00	3.00
Volume 1 M HCl (mL)	0.30	0.50	0.80
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
% Yb recovered in solid	99	97	82

Table 16: Yb(III) reduction in CH_3CN with HOAc.

Components	**I-89**	**I-90**	**I-91**
Volume CH_3CN (mL)	3.00	3.00	3.00
Volume 1 M HOAc (mL)	0.30	0.50	0.80
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
% Yb recovered in solid	75	36	42

present. However, each reaction produced colorless crystals with no evidence of the formation of Yb(II).

Due to the large amount of Yb recovered in the acetonitrile/HCl system (Table 15), experiments were performed to determine the behavior of $LuCl_3 \cdot 8H_2O$ in the same system. Reactions I-86 through I-88 were repeated with $LuCl_3 \cdot 8H_2O$ instead of $YbCl_3 \cdot 8H_2O$. Each reaction was performed in triplicate and allowed to react at room temperature for 36 hours. A tan solution and tan precipitate formed in each reaction. Table 17 contains the components of each reaction and the % Lu that remained in solution. According to Table 17, some Lu was retained in the liquid phase, suggesting $LuCl_3$ is somewhat insoluble in this medium.

Further experimentation with this system involved adding sulfate to a divalent form of Yb in order to form $YbSO_4$. Yb(II) was first produced as the chloride by allowing 3 mL CH_3CN, 0.3 mL 1 M HCl, 0.04 g $YbCl_3 \cdot 8H_2O$, 0.04 g NaTPB, and a strip

Table 17: Lu(III) reactions in CH_3CN.

Components	**I-92**	**I-93**	**I-94**
Volume CH_3CN (mL)	3.00	3.00	3.00
Volume 1 M HCl (mL)	0.30	0.50	0.80
Mass NaTPB (g)	0.04	0.04	0.04
Mass $LuCl_3 \cdot 6H_2O$ (g)	0.0037	0.0037	0.0037
% Lu retained in solution	57	43	48

Table 18: Yb(III) reduction in CH_3CN with HCl, addition of 1.0 M Na_2SO_4.

Components	**I-95**	**I-96**	**I-97**
Volume CH_3CN (mL)	3.00	3.00	3.00
Volume 1 M HCl (mL)	0.30	0.50	0.80
Volume 1 M Na_2SO_4	1.00	2.00	3.00
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
% Yb recovered in solid	98	99	99

of abraded Mg ribbon to react at room temperature for 36 hours. Each reaction was performed in triplicate and each resulted in a tan solution and a green precipitate. The solid and liquid were separated via centrifugation and the supernatant removed. Varying amounts of 1 M Na_2SO_4 solution were added to the precipitate and allowed to stir for one week at room temperature (I-95 through I-97). The components and % Yb recovered in the solid phase are included in Table 18. Each reaction resulted in an intense green precipitate, similar to that formed in reactions I-38 through I-40.

Due to the large percent recovery of Yb in the solid phase, the feasibility of the separation process in CH_3CN and HCl with the sulfate addition was examined. Reactions 1-95, I-96, and I-97 were repeated with $LuCl_3 \cdot 6H_2O$ instead of $YbCl_3 \cdot 8H_2O$. An intial experiment was performed by allowing 3 mL CH_3CN, 0.3 mL 1 M HCl, 0.04 g $LuCl_3 \cdot 6H_2O$, 0.04 g NaTPB, and a strip of abraded Mg ribbon to react at room temperature for 36 hours. Each reaction was performed in triplicate and each resulted in

Table 19: Lu(III) in CH_3CN with HCl, addition of 1.0 M Na_2SO_4.

Components	**I-98**	**I-99**	**I-100**
Volume CH_3CN (mL)	3.00	3.00	3.00
Volume 1 M HCl (mL)	0.30	0.50	0.80
Volume 1 M Na_2SO_4	1.00	2.00	3.00
Mass NaTPB (g)	0.04	0.04	0.04
Mass $LuCl_3 \cdot 6H_2O$ (g)	0.04	0.04	0.04
% Lu retained in solution	86	84	83

a tan solution and a tan precipitate. The solid and liquid were separated via centrifugation and the supernatant removed. Varying amounts of 1 M Na_2SO_4 solution were added to the precipitate and allowed to stir for one week at room temperature (I-98 , I-99, I-100). Table 19 contains the components of the reactions and the % Lu that remained in solution. Each reaction resulted in a tan solution with a tan precipitate. According to the data collected, a significant amount of Lu is present in the precipitate.

When separate Yb and Lu experiments are performed in CH_3CN with the addition of sulfate, they do not appear to be separable, as $YbSO_4$ and $Lu_2(SO_4)_3$ are both insoluble. An experiment was performed (I-101), in triplicate and allowed to react at room temperature for 36 hours, to determine the solubility of the sulfates in this system. It was speculated the TPB would protect Yb(II) and allow for the precipitation of $YbSO_4$ and in turn this would prevent the precipitation of $Lu_2(SO_4)_3$. Table 20 lists the components of the experiment and the amount of Yb recovered in the solid phase and the amount of Lu recovered in the liquid phase. Each sample produced a tan solution with a green precipitate. According to the data collected in Table 20, the separation of Yb and Lu in CH_3CN is not feasible under these conditions.

Previous work in the laboratory has shown the reduction of Yb(III) can be achieved by adding saturation amounts of $YbCl_3 \cdot 8H_2O$ (~0.35 g) to 1.5 mL 1:1

Table 20: Yb(III) and Lu(III) in CH_3CN system.

Components	**I-101$_1$**	**I-101$_2$**	**I-101$_3$**
Volume CH_3CN (mL)	3.00	3.00	3.00
Volume 1 M HCl (mL)	0.30	0.30	0.30
Mass NaTPB (g)	0.04	0.04	0.04
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.04	0.04	0.04
Mass $LuCl_3 \cdot 6H_2O$ (g)	0.0037	0.0037	0.0037
% Yb recovered in solid	70	57	64
% Lu retained in solution	48	50	45

EtOH:1,4-dioxane, a drop of glacial acetic acid, and a sufficient amount of Mg powder. A yellow-green solution, presumably Yb(II) forms almost immediately. However, this reduced form of Yb only persists for approximately 5 minutes. When the reaction undergoes ultrasonic treatment for 20 minutes, a yellow-green solid forms, presumably Yb(II) as the chloride. Exposure of this solid to air results in almost immediate oxidation of Yb(II) to Yb(III). New experiments were performed to ensure that Yb(II) can be reproducibly generated using this system. In reaction I-102, approximately 0.20 g Mg powder were added to a solution containing 0.35 g $YbCl_3 \cdot 8H_2O$ dissolved in 0.75 mL 95% EtOH , 0.75 mL 1,4-dioxane, and 0.05 mL glacial acetic acid. This reaction was performed in triplicate at room temperature and resulted in a yellow-green solution that formed almost immediately and persisted for up to 6 minutes. Reaction I-103 had the same components as I-102, but was exposed to ultrasonic treatment for 20 minutes. The reaction was performed in triplicate, with the water temperature of the sonicator set at 25º C. Each reaction resulted in the formation of a yellow-green precipitate that persisted for up to 20 minutes. Removal of the supernatant and exposure of this solid to air resulted in an almost immediate oxidation of Yb(II) to Yb(III), as the solid turned white.

Previous experiments and the literature suggest the half-life of Yb(II) in the presence of NaTPB is drastically increased. The next modification to this system was addition of the stabilizing agent NaTPB. In reaction I-104, approximately 0.20 g Mg powder were added to a solution containing 0.35 g $YbCl_3 \cdot 8H_2O$ and 0.35 g NaTPB dissolved in 0.75 mL 95% EtOH , 0.75 mL 1,4-dioxane, and 0.05 mL glacial acetic acid. This reaction was performed in triplicate and allowed to react at room temperature. Each of the reactions resulted in a colorless solution which then turned cloudy, with no evidence of the formation of Yb(II). Reaction I-105 contained the same components as I-104 but was exposed to ultrasonic treatment for 20 minutes. The reaction was performed in triplicate, with the water temperature of the sonicator set at 25 ºC. Each reaction resulted in a white precipitate, with no evidence of the formation of Yb(II).

A stable form of Yb(II) was not produced in reactions I-102 through I-105. The next modification to this system was repeating these reactions in different organic solvents. The literature suggests tetrahydrofuran (THF) is the best known solvent for lanthanide reduction. Reactions I-102 through I-105 were repeated with THF and 1,4-dioxane instead of EtOH and 1,4-dioxane. Each produced results identical to those performed with EtOH. Another alternative solvent system was EtOH and 1,3-dioxolane. Again, these were similar to the results obtained with the EtOH:1,4-dioxane system.

Removal of the yellow-green Yb(II) from Mg powder (I-102) resulted in an almost immediate oxidation to Yb(III). The preparation of Yb(II) was further examined to determine if a more stable solution could be prepared. It was discovered a ratio of 3:1 EtOH:1,4-dioxane produced a more intensely colored green solution, indicating more Yb(II) present.

The next step in this research was to revert to the precipitation of $YbSO_4$ using a different sulfate source. The first sulfate, $(NH_4)_2SO_4$, was chosen because of its tendency to be highly soluble in aqueous media. Yb(II) was prepared by adding approximately 0.20 g Mg powder to a solution containing 0.35 g $YbCl_3 \cdot 8H_2O$ dissolved in 0.75 mL 95% EtOH, 0.75 mL 1,4-dioxane and 0.05 mL glacial acetic acid. Attempts were made to precipitate $YbSO_4$ by adding 1 mL of the Yb(II) solution to a test tube containing 0.5 mL saturated $(NH_4)_2SO_4$ solution. This reaction (I-106) was performed in triplicate and allowed to react at room temperature. Within five minutes, the once green solution/precipitate turned colorless/white. This setup was further modified by varying the amounts and concentrations of the $(NH_4)_2SO_4$ solution used. Table 21 contains the amounts and components of each reaction performed using 0.5 M $(NH_4)_2SO_4$ in this system (I-107, I-108, I-109). Each reaction resulted in the formation of a white precipitate, indicating $YbSO_4$ had not formed. Table 22 contains the amounts and components of each reaction performed using 1.0 M $(NH_4)_2SO_4$ in this system (I-110, I-111, I-112). Each reaction resulted in the formation of a white precipitate, indicating $YbSO_4$ had not formed. Table 23 contains the amounts and components of each reaction performed using 1.5 M $(NH_4)_2SO_4$ (I-113, I-114, I-115). Each reaction resulted in the formation of a green precipitate that turned white within a few minutes, indicating a stable form of $YbSO_4$ had not been produced.

The next modification to this system was the addition of Na_2SO_3 instead of $(NH_4)_2SO_4$. This was employed because the sulfur in Na_2SO_3 is a lower oxidation state than in $(NH_4)_2SO_4$, which would hopefully hinder the oxidation of Yb(II). Attempts were made to precipitate $YbSO_4$ by adding 1 mL Yb(II) [as previously prepared] to a test tube

Table 21: Yb(II) addition to 0.5 M $(NH_4)_2SO_4$.

Components	**I-107**	**I-108**	**I-109**
Volume 95% EtOH (mL)	0.75	0.75	0.75
Volume 1,4-dioxane (mL)	0.75	0.75	0.75
Volume HoAC (mL)	0.05	0.05	0.05
Volume 0.5 M $(NH_4)_2SO_4$ (mL)	1.00	2.00	3.00
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.35	0.35	0.35
Mass Mg powder (g)	0.20	0.20	0.20

Table 22: Yb(II) addition to 1.0 M $(NH_4)_2SO_4$.

Components	**I-110**	**I-111**	**I-112**
Volume 95% EtOH (mL)	0.75	0.75	0.75
Volume 1,4-dioxane (mL)	0.75	0.75	0.75
Volume HoAC (mL)	0.05	0.05	0.05
Volume 1.0 M $(NH_4)_2SO_4$ (mL)	1.00	2.00	3.00
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.35	0.35	0.35
Mass Mg powder (g)	0.20	0.20	0.20

Table 23: Yb(II) addition to 1.5 M $(NH_4)_2SO_4$.

Components	**I-113**	**I-114**	**I-115**
Volume 95% EtOH (mL)	0.75	0.75	0.75
Volume 1,4-dioxane (mL)	0.75	0.75	0.75
Volume HoAC (mL)	0.05	0.05	0.05
Volume 1.5 M $(NH_4)_2SO_4$ (mL)	1.00	2.00	3.00
Mass $YbCl_3 \cdot 8H_2O$ (g)	0.35	0.35	0.35
Mass Mg powder (g)	0.20	0.20	0.20

containing 0.5 mL 0.4 M Na_2SO_3 solution. Each reaction was performed in triplicate at room temperature (I-116). A green precipitate, which persisted for a short time longer than that which was produced with $(NH_4)_2SO_4$, formed for each reaction. Further investigation of this system led to the conclusion that Yb(II) was reducing Na_2SO_3 to sulfur, as the potential of the SO_3^{-2}/ S couple is 0.18 V and that of Yb^{+3}/Yb^{+2} is ~-1.1 V.

This system was further modified by using an organic sulfate as the precipitating agent. Compounds such as tetramethylammonium methyl sulfate (TMAMS) and tetramethylammonium sulfate (TMAS) will dissolve more readily in an organic solvent, which eliminates the addition of excessive amounts of water to the system. Less water might produce stable $YbSO_4$ that can persist in air for an extended period of time. Attempts were made to precipitate $YbSO_4$ by adding Yb(II) [as previously prepared] to a test tube containing TMAMS, which was dissolved in a mixture containing varying amounts of EtOH, 1,4-dioxane, water, and acetic acid. Table 24 contains the amounts of the components and Table 25 contains the observations of each reaction. The reactions were performed in triplicate and allowed to react at room temperature. A stable $YbSO_4$ precipitate was not formed in any reaction with TMAMS.

Table 24: Yb(II) addition to TMAMS

Components	**I-117**	**I-118**	**I-119**	**I-120**	**I-121**
Volume EtOH (µL)	100	100	0	100	100
Volume 1,4-dioxane (µL)	100	100	0	100	100
Volume H_2O (µL)	100	100	0	0	0
Volume HOAc (µL)	0	50	50	0	50
Mass TMAMS (g)	0.05	0.05	0.05	0.05	0.05
Volume Yb(II) (µL)	1000	1000	1000	1000	1000

Table 25: Observations of Yb(II) addition to TMAMS

Sample	**Observations**
I-117	clear green solution
I-118	green precipitate turned white after 3 minutes
I-119	white precipitate
I-120	green precipitate turned white after 3 minutes
I-121	clear green solution

Reactions (I-122 through I-126) were then performed with TMAS instead of TMAMS. Table 26 contains the amounts of the components and Table 27 contains the observations of each reaction. The reactions were performed in triplicate and allowed to react at room temperature. Green $YbSO_4$ formed in each reaction that contained TMAS.

The use of TMAS as the precipitating agent resulted in a more stable green precipitate than any previous system. The next step was to determine the activity of Yb(III) in this system. A successful separation could possibly be achieved if Yb(III) would remain soluble and Yb(II) precipitate as the sulfate. This would indicate Lu(III) might remain in solution. Two reactions were performed with either Yb(III) or Yb(II) that allowed us to ascertain the solubility of each in this system. Yb(II) was prepared as previous reactions indicate and Yb (III) was prepared in a similar manner without the reduction. The amounts of the components and observations with Yb(III) are listed in Table 28 (I-127, I-128), and those for Yb(II) are listed in Table 29 (I-129, I-130). Each reaction was performed in triplicate and allowed to react at room temperature. Each reaction performed with Yb(III) resulted in a clear, colorless solution with no precipitate and those with Yb(II) resulted in a light green precipitate that turned white within five minutes. The observations indicate a feasible system for the separation of Yb(II) and Lu(III) with the use of TMAS could be possible.

Table 26: Yb(II) addition to TMAS.

Components	**I-122**	**I-123**	**I-124**	**I-125**	**I-126**
Volume EtOH (µL)	100	100	0	100	100
Volume 1,4-dioxane (µL)	100	100	0	100	100
Volume H_2O (µL)	100	100	0	0	0
Volume HOAc (µL)	0	50	50	0	50
Mass TMAS (g)	0.05	0.05	0.05	0.05	0.05
Volume Yb(II) (µL)	1000	1000	1000	1000	1000

Table 27: Observations of Yb(II) addition to TMAS.

Sample	**Observations**
I-122	light green precipitate turned white after 5 minutes
I-123	light green precipitate turned white after 3 minutes
I-124	light green precipitate turned white after 5 minutes
I-125	light green precipitate turned white after 5 minutes
I-126	light green precipitate turned white after 3 minutes

Table 28: Yb(III) addition to TMAS.

Components	**I-127**	**I-128**
Volume EtOH (µL)	100	100
Volume 1,4-dioxane (µL)	100	100
Volume H_2O (µL)	100	100
Volume HOAc (µL)	0	50
Mass TMAS (g)	0.05	0.05
Volume Yb(III) (µL)	1000	1000
Observations	clear, colorless solution	clear, colorless solution

Table 29: Yb(II) addition to TMAS with Observations.

Components	**I-129**	**I-130**
Volume EtOH (µL)	100	100
Volume 1,4-dioxane (µL)	100	100
Volume H_2O (µL)	100	100
Volume HOAc (µL)	0	50
Mass TMAS (g)	0.05	0.05
Volume Yb(II) (µL)	1000	1000
Observations	clear, colorless solution	clear, colorless solution

Further investigations in this research involved creating an optimal system that would precipitate the largest amount of Yb(II) that persisted for a lengthy amount of time. Varying amounts, concentrations, and ratios of the TMAS, EtOH, 1,4-dioxane, and water were all investigated. Tables 30, 31, 32, and 33 contain the amounts of the components of each reaction, as well as the observations. Each reaction was performed in triplicate and allowed to react at room temperature. Overall, reactions I-140 through I-142 yielded the best results, as all of the reactions resulted in the precipitation of green $YbSO_4$ that persisted for over an hour.

Further alterations to this research involved increasing the amount of TMAS to see if a larger amount of precipitate, namely $YbSO_4$, would form. Reaction I-143 contained the same amounts and components as I-142, but with 0.2 g TMAS. This

Table 30: Yb(II) addition to TMAS dissolved in EtOH:1,4-dioxane:H_2O and HOAc.

Components	**I-131**	**I-132**	**I-133**
Volume EtOH (µL)	165	165	165
Volume 1,4-dioxane (µL)	165	165	165
Volume H_2O (µL)	165	165	165
Volume HOAc (µL)	50	50	50
Mass TMAS (g)	0.02	0.05	0.10
Volume Yb(II) (µL)	500	500	500
Observations	white precipitate	green precipitate	green precipitate

Table 31: Yb(II) addition to TMAS dissolved in EtOH:1,4-dioxane:H_2O (1).

Components	**I-134**	**I-135**	**I-136**
Volume EtOH (µL)	165	165	165
Volume 1,4-dioxane (µL)	165	165	165
Volume H_2O (µL)	165	165	165
Mass TMAS (g)	0.02	0.05	0.10
Volume Yb(II) (µL)	500	500	500
Observations	white precipitate	light green precipitate	green precipitate

Table 32: Yb(II) addition to TMAS dissolved in EtOH:1,4-dioxane:H_2O (2).

Components	**I-137**	**I-138**	**I-139**
Volume EtOH (µL)	375	375	375
Volume 1,4-dioxane (µL)	125	125	125
Volume H_2O (µL)	250	250	250
Mass TMAS (g)	0.02	0.05	0.10
Volume Yb(II) (µL)	500	500	500
Observations	white precipitate	white precipitate	white precipitate

Table 33: Yb(II) addition to TMAS dissolved in EtOH:1,4-dioxane:H_2O (3).

Components	**I-140**	**I-141**	**I-142**
Volume EtOH (µL)	150	150	150
Volume 1,4-dioxane (µL)	50	50	50
Volume H_2O (µL)	100	100	100
Mass TMAS (g)	0.02	0.05	0.10
Volume Yb(II) (µL)	1000	1000	1000
Observations	green precipitate	green precipitate	green precipitate

reaction was performed in triplicate an allowed to react at room temperature. A substantially greater amount of $YbSO_4$ was recovered, which persisted for over an hour.

When the reduction of Yb(III) to Yb(II) is performed in air, oxygen is a competing factor that limits the amount of Yb(II) that can actually be obtained. Therefore, reaction I-143 was repeated in a glove bag filled with nitrogen. This reaction was performed in triplicate and allowed to react at room temperature. Each reaction resulted in a darker green precipitate, an intensity that had not been seen up to this point in this research. AE analysis showed approximately 26% Yb was recovered in the solid phase. Additional reactions were performed with increasing amounts of solvent and varying amounts of TMAS to determine if a larger percentage of Yb can be recovered in the solid phase. Table 34 contains the amounts and components of each reaction and the

Table 34: Yb(II) addition to TMAS dissolved in EtOH:1,4-dioxane:H_2O (4).

Components	**I-144**	**I-145**	**I-146**	**I-147**
Volume EtOH (µL)	450	450	450	450
Volume 1,4-dioxane (µL)	150	150	150	150
Volume H_2O (µL)	300	300	300	300
Mass TMAS (g)	0.05	0.10	0.15	0.2
Volume Yb(II) (µL)	1000	1000	1000	1000
% Yb recovered in solid	52	69	88	82

% Yb recovered in the solid phase. Each reaction was performed in triplicate and allowed to react at room temperature in a glove bag filled with nitrogen.

A significant amount of Yb was recovered in the solid phase in reaction I-146. Therefore, this was repeated three more times in order to determine if this system was reproducible. An average of 83% Yb was recovered in the solid phase. Due to the significant amounts of Yb recovered, experiments were performed to determine the feasibility of the system for the separation of Yb(II) and Lu(III). Reaction I-148 contained the same components as I-146, except Yb(III) solution was added instead of Yb(II). A clear, colorless solution resulted with no evidence of a precipitate. This indicates Lu(III) might remain in solution, while Yb(II) is insoluble, in this system.

Further modifications to this research involved constructing an apparatus that allowed the reaction to take place under nitrogen, without the use of a glove bag. Figure 5 is an illustration of this system. Yb(III) solution was prepared by dissolving 0.35 g $YbCl_3 \cdot 8H_2O$ in 0.75 mL 95% EtOH, 0.75 mL 1,4-dioxane and 0.05 mL glacial acetic acid. The solution was then added to a column containing approximately 8 g Mg powder. An aspirator was used to pull the Yb(III) solution through the Mg which was reduced to Yb(II). The Yb(II) solution then dripped into a flask containing 0.15 g TMAS dissolved

in 0.45 mL EtOH, 0.15 mL 1,4-dioxane, and 0.3 mL water (I-149), resulting in the formation of a green precipitate. However, within three to five minutes, complete evaporation occurred resulting in a white precipitate. Pulling a vacuum on the system posed a problem with evaporation of the solvent and immediate oxidation of the Yb(II) to Yb(III). Therefore, an alternate system was devised. Figure 6 is an illustration of the apparatus that was employed in order to avoid evaporation of the solvent. Yb(III) solution [as previously prepared] was added to the column via a syringe through the septum. The flow of nitrogen was used to push the Yb(III) through the Mg column, which was then reduced to Yb(II). The Yb(II) solution dripped into the flask which contained 0.15 g TMAS dissolved in 0.45 mL EtOH, 0.15 mL 1,4-dioxane, and 0.3 mL water (I-151). A green precipitate formed almost immediately. However, a build-up of pressure resulted from the formation of H_2 gas. Modifications were made to this setup that allowed for nitrogen input, a vent to release the pressure, and an inlet to allow for more Yb(III) solution to be added. Figure 7 is an illustration of the apparatus that was employed to eliminate the problems associated with the evolution of H_2 gas. A green precipitate formed, but the system was such that the evolution of H_2 gas could not be adequately controlled.

The next modification to this research was to devise a simple system that allowed for the reduction/separation process. Figure 1 is an illustration of this apparatus. In reaction I-152, Yb(III) solution [as previously prepared] was added to a test tube that had been flushed with nitrogen and contained 0.5 g TMAS and 0.2 g Mg powder by the use of a syringe through the septum. The reaction was performed in triplicate and allowed to react at room temperature for 15 minutes. The TMAS was not dissolved in the 3:1:2

mixture of EtOH:1,4-dioxane:water to determine if the precipitation of $YbSO_4$ still occurs. The reduction of Yb(III) to Yb(II) was seen immediately, as indicated by a green solution, and a green precipitate formed almost immediately. Reaction I-152 was then repeated, except the reaction time was increased to 30 minutes (I-153). This was done to determine if time has an effect on the amount of Yb(II) recovered. Again, Yb(III) reduction occurred and a green precipitate formed. The amount of Yb recovered in the solid phase is listed in Table 35. AE analysis showed the increased reaction time has no effect on the amount of Yb recovered in the solid phase.

During the summer months, the temperature in the lab was approximately 30 ºC. It was quickly determined an increased temperature greatly affects the reduction of Yb(II). The intensity and longevity of the Yb(II) solution produced was much less than before, as the green Yb(II) was oxidizing to Yb(III) in less than a minute. Therefore, Yb(III) solution [as previously prepared] was added to a test tube that had been flushed with nitrogen and contained Mg powder. This reaction was performed over dry ice. The reduction of Yb(III) to Yb(II) occurred, as an intense green solution that formed persisted for several minutes. However, it was discovered the solution is freezing. Therefore, this reaction was performed over ice. A green solution formed immediately and persisted for

Table35: Timed Yb(II) addition to TMAS.

Components	**% Yb recovered in solid**
$I\text{-}152_1$ (15)	67
$I\text{-}152_2$ (15)	72
$I\text{-}152_3$ (15)	53
$I\text{-}153_1$ (30)	47
$I\text{-}153_2$ (30)	68
$I\text{-}153_3$ (30)	67

several minutes. In reaction (I-154), Yb(III) solution [as previously prepared] was added to a test tube flushed with nitrogen that contained 0.15 g TMAS and 0.20 g Mg powder. The reaction was allowed to sit in ice for 5 minutes with occasional agitation. This reaction was performed in triplicate. Each reaction resulted in the formation of a bright green solution with a bright green precipitate that persisted for several hours.

The next factor investigated for this system was reaction time. Reaction I-155 was performed in triplicate and allowed to sit in ice for 15 minutes with occasional agitation. Each reaction resulted in the formation of a bright green solution with a bright green precipitate. AE analysis showed approximately 52% Yb was recovered in the solid. Reaction I-156 was performed in triplicate and allowed to sit in ice for 30 minutes with occasional agitation. Each reaction resulted in the formation of a bright green solution with a bright green precipitate. AE analysis showed approximately 61% Yb was recovered in the solid. Reaction I-157 was performed in triplicate and allowed to sit in ice for 60 minutes with occasional agitation. Each reaction resulted in the formation of a pale yellow solution with a significantly large amount of bright green precipitate. AE analysis showed approximately 74% Yb was recovered in the solid.

Increasing the reaction time increased the amount of Yb recovered in the solid and cooling the system greatly increased the intensity and longevity of the green precipitate. However, upon centrifugation, a sizable amount of Yb(II) was lost, likely due to an increase in temperature in the centrifuge. A test tube containing ice water (0 ºC) was centrifuged for 5 minutes to ascertain the loss of Yb(II) was due to the heat generated from the centrifuge. After this time, the temperature of the solution had increased 16 ºC. Further experiments were centrifuged with a piece of dry ice in the

bottom of the chamber. Reaction I-157 was repeated in triplicate and then centrifuged with a piece of dry ice. AE analysis showed a maximum of 85% Yb was recovered in the solid phase.

The next modification to this system was devising a method to remove the solution from the precipitate. An initial technique was removing the solution through a cotton-plugged syringe. In order for this to happen, the septum was removed and the system was exposed to air. An immediate oxidation of Yb(II) to Yb(III) occurred, resulting in less recovery of Yb in the solid. An apparatus was devised that would allow for removal of the solution without exposure to air. Figure 2 is an illustration of this setup. However, due to the small size of the opening of the test tube, it was very difficult to perform the tasks of adding the Yb(III) solution, venting, and flushing with nitrogen. Therefore, another apparatus was developed. Figure 3 is an illustration of this setup. The three different openings allowed for easier injection of the solution, venting, and flushing with nitrogen. This vessel was too large for the quantities of materials that showed previous success, as the formation of $YbSO_4$ did not occur. A new apparatus was designed that consisted of a test tube attached to the bottom of a 25 mL 3-neck round bottom flask. This allowed for the three openings and a small area for the reaction to take place. This is shown in figure 4. The formation of $YbSO_4$ occurred, but removal of the solution still posed problems. A smaller apparatus was constructed with a 15 mL 3-neck round bottom flask. Again, green $YbSO_4$ formed, but removal of the solution was still an issue yet to be solved.

Chapter 4

CONCLUSION

The aim of this research was to attempt to develop an industrial process for the separation of Lu and Yb. The proposed mechanism was to reduce Yb(III) to Yb(II) under conditions that would not reduce Lu(III) to Lu(II). Advantage was then to be taken of the differences in the chemistry of Yb(II) and Lu(III) to effect a separation.

Previous electrolytic reductions of Yb(III) to Yb(II) were obtained through the use of either a Hg cathode or a Hg amalgam. However, due to the severe toxicity of Hg, its use in an industrial setting is prohibited. Therefore, Mg, which is a safe alternative and has the potential to reduce Yb(III) to Yb(II), was used throughout this research as the reducing agent.

The most effective system, which could be industrialized, was the following. Approximately 0.35 g $YbCl_3 \cdot 8H_2O$ were dissolved in 1.5 mL of 3:1 EtOH:1,4-dioxane and 0.05 mL 17.4 M acetic acid. This solution was added to 0.15 g TMAS and approximately 0.20 g Mg powder under nitrogen and over ice. The system could be relied upon to produce approximately 85% separation.

The major difficulty in bringing about the separation is the production and persistence of Yb(II). The Yb(III)/Yb(II) potential is ~-1.1 V which indicates that the Yb(II) species is oxidized by water, by hydrogen ion, and by oxygen in the air. This difficulty appears to have been partially solved by the use of mixed aqueous/non-aqueous media. The present research points the way forward to further investigations which would both simplify the procedure and increase the percent yield of separated Yb(II).

LIST OF REFERENCES

1. Melcher, C.L., “International Workshop on Heavy Scintillators for Scientific and Industrial Applications”, Editions Frontiers, Gif – Sur – Yvette, France, 1993.
2. Greenwood, N.N., Earnshaw, A., “Chemistry of the Elements”, Pergammon Press, New York, New York, 1984, Chapter 30, p. 1227,1232.
3. Bard, A.J., Parsons, R., Jordan, J., “Standard Potentials in Aqueous Solution”, Marcel Dekker, Inc., New York, New York, 1985, Chapter 20, p. 624.
4. Powell, J.E., “Handbook on the Physics and the Chemistry of Rare Earths”, North Holland Publishing Company, New York, New York, 1979, Chapter 22+.
5. Nash, K. L.; Jensen, M. P. “Handbook on the Physics and Chemistry of Rare Earths”;North-Holland Publishing Company, Elsevier: North-Holland, N.Y., 2000; Chapter 180.
6. Klemm, W., Schüth, W., Zeitschrift Anorganische und Allegemeine Chemie, **184**, 352-358, (1929).
7. Yntema, L.F., Ball, R.W., Journal of the American Chemical Society, **52**, 4264-4268, (1930).
8. Prandtl, V.W., Zeitschrift Anorganische und Allegemeine Chemie, **209**, 13-16, (1932).
9. Pearce, D.W., Naesar, C.R., Hopkins, B.S., Transactions of Electrochemical Society, **69**, 557-565, (1936).
10. Marsh, J.K., Journal of the Chemical Society, 1367-1368, (1937).
11. Brukl, A., Angewandte Chemie, **50**, 25-29, (1937).
12. Holleck, L., Noddack, W., Angewandte Chemie, **50**, 819-824, (1937).
13. Holleck, L., Angewandte Chemie, **51**, 243-251, (1938).

14. Walters, G.C., Pearce, D.W., Journal of the American Chemical Society, 62, 3330-3332, (1940).

15. Laitinen, H.A., Journal of the American Chemical Society, **64**, 1133-1135, (1942).

16. Johnson, D.A., Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry, **16**, 1671-1675, (1974).

17. Morss, L.R., Chemical Reviews, **6**, 827-842, (1976).

18. Ferri, D., Salvatore, F., Annali di Chimica, **78**, 431-440, (1988).

19. Peltier, M., Rombau, P., French Patent, Fr. 1,209,251, (1960).

20. Asprey, L.B., Ellinger, F.H., Staritzky, E., Proceedings – Conference on Rare Earth Research, **3**, 11-20, (1964).

21. Mikheev, N.B., *et al.*, Inorganic and Nuclear Chemistry Letters, **8**, 523-528, (1972).

22. Maksai, L.I., Sayun, M.G., VINITI, 185-196, (1974).

23. Myasoedov, B.F., Kulyako, Y.M., Sklyarenko, I.S., Radiokhimiya, **17**, 434-440, (1975).

24. Kamenskaya, A.N., *et al.*, Russian Journal of Inorganic Chemistry, **28**, 965-968, (1983).

25. Valeshko, I.E., Mikheev, N.B., Kulyukhin, S.A., Radiokhimiya, **34**, 49-57, (1992).

26. Kulyukhin, S.A., *et al.*, Radiokhimiya, **34**, 57-61, (1992).

27. Hanamoto, T., Sugimoto, Y., Sugino, A., Inanaga, J., Synlett, **5**, 377-378, (1994).

28. Siler, J.D. “The Reduction of Yb(III) to Yb(II) using Magnesium”, The University of Tennessee, Knoxville, TN, M.S. Thesis, 1998.

29. Clifford, A.F., Beachell, H.C., Journal of the American Chemical Society, **70**, 2730-2731, (1948).

30. Mack, R.J. “Reduction of Yb(III) to Yb(II) to Separate Yb from other Lanthanides”, The University of Tennessee, Knoxville, TN, M.S. Thesis, 2000.

31. Bard, A.J., Parsons, R., Jordan, J., “Standard Potentials in Aqueous Solution”, Marcel Dekker, Inc., New York, New York, 1985, Chapter 22, p. 699.

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